

PATENT
12598.0144.NPUS00
14-54(14065)
SOLU:144

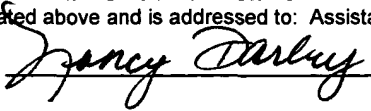
APPLICATION FOR UNITED STATES LETTERS PATENT

For

**PROCESS FOR REMOVAL OF ACROLEIN FROM ACRYLONITRILE
PRODUCT STREAMS**

By

**Gregory J. Ward, Bryan C. Blanchard, Scott G. Moffatt, Valerie S. Monical,
Richard D. Murphy and Balshekar Ramchandran**

EXPRESS MAIL MAILING LABEL	
NUMBER	<u>EV 318623052 US</u>
DATE OF DEPOSIT	<u>JUNE 27, 2003</u>
I hereby certify that this paper or fee is being deposited with the United States Postal Service "EXPRESS MAIL POST OFFICE TO ADDRESSEE" service under 37 C.F.R. 1.10 on the date indicated above and is addressed to: Assistant Commissioner for Patents, Washington D.C. 20231.	
<u></u>	
Signature	

BACKGROUND OF THE INVENTION

This invention relates to the purification of acrylonitrile. More particularly, it relates to removal of acrolein from acrolein-containing acrylonitrile process streams by reaction of the acrolein with a scavenger compound to produce an acrolein derivative.

Acrylonitrile is a well-known article of commerce widely used in the manufacture of synthetic resins and fibers and as a valuable intermediate in the synthesis of many organic compounds. In most large-scale industrial processes for producing this nitrile, minor amounts of undesired byproducts and contaminants, including acetone, acrolein, acetaldehyde, and other similar carbonyl compounds, are simultaneously produced.

In most commercial applications utilizing acrylonitrile as a starting material, it is critical that the starting material be in as pure a state as possible as even minute traces of impurities can cause extremely low production yields and/or inferior end product quality. This impact is particularly prevalent when acrylonitrile is used in the preparation of synthetic resins and fibers.

The presence of even very small trace quantities of acrolein renders the acrylonitrile unsuitable for many applications. For example, acrolein can act as a crosslinker or an alkylol adduct with acrylamide when the nitrile is converted to acrylamide and then polymerized, such as for eventual end-use as a fiber or flocculent. The presence of acrolein contaminant can thereby result in polyacrylamide that is of insufficient molecular weight or which contains undesirable insoluble material. Thus, it is essential for many end uses that acrolein concentrations in acrylonitrile starting materials, if any, be reduced to below 15 ppm, more preferably 5 ppm or less, by weight of the commercial grade acrylonitrile if it is to be successfully marketed.

Although prior art commercial acrylonitrile production systems typically include purification steps often using distillation processes, acrolein reduction to this required level is difficult. More specifically, prior art methods for removal of acrolein from the crude acrylonitrile stream have typically involved pH adjustments and/or control at various points in the process which add cost or have undesirable impact such as side reaction catalysis and equipment fouling. In U.S. 3,185,636 to Stevens et al, the absorber column pH is maintained at a substantially neutral or slightly alkaline pH, whereby the saturated carbonyl compounds in the reactor effluent combine with the excess hydrogen

1 cyanide to form the corresponding cyanohydrin. In U.S. 3,462,477 to Caporali et al a pH
2 of between 7.5 and 11 was required to separate the acrolein from the crude acrylonitrile
3 by distillation. In published EP application 0110861, acrolein is removed by maintaining
4 the pH in the zone of maximum acrolein concentration of the recovery column at from
5 about 5.25 to 7.

6 Other attempts to separate acrolein and other byproducts from acrylonitrile have
7 not successfully reduced the acrolein content to the required level. In U.S. 3,328,266 to
8 Modiano et al the crude acrylonitrile stream from the absorber with a pH generally
9 between 9 and 9.5 is subjected to extractive distillation apparently without any further
10 adjustment of pH. The acrolein content remains high, however, even after the third stage
11 of the distillation is completed and does not produce acrylonitrile of sufficient purity for
12 fiber production.

13 The separation of acrylonitrile from acetonitrile and small quantities of acrolein is
14 discussed in U.S. 3,459,639 to Borrel et al. Under the disclosed conditions for the
15 distillation recovery column, the acrolein was not significantly affected and remained
16 above 200 parts per million in the separated organic product phase.

17 Yet other prior art acrolein removal processes utilize additives to improve and
18 increase acrolein reduction. For example, U.S. Patent No. 5,760,283 describes the
19 addition of strong bases in the recovery section of the process while U.S. Patent No.
20 6,074,532 describes adding a substituted aromatic amine prior to distillation. These types
21 of processes add significant cost to the overall process and have the potential to catalyze
22 unwanted side reactions and to form undesirable byproducts.

23 Japanese application no. 53-60040 describes the removal of acrolein with an ion
24 exchange resin. Accordingly, there continues to be an unmet need for an inexpensive and
25 effective process for removal of acrolein from process streams that achieves the purity
26 levels critical for use of these process streams.

27

Summary Of The Invention

This invention provides a process for the removal of sufficient amounts of acrolein from acrolein-containing process streams to result in reduction of the acrolein content to less than about 15 and preferably less than 5 parts per million.

An object of the present invention is, therefore, to provide an inexpensive process for removing acrolein from an unrefined acrolein-containing process stream.

Another object of the present invention is to provide a process for removing acrolein from an unrefined acrolein-containing process stream that reduces acrolein levels to below the level critical for commercial use, preferably in conjunction with acrylonitrile-containing process streams usable in polymerization processes.

Another object of the present invention is to provide a process for removing acrolein from an unrefined acrolein-containing process stream without generating unwanted by-products or contaminants as part of the process.

The invention achieves these and other desirable objectives by providing a process for removal of acrolein from an acrolein-containing process stream that includes reacting the acrolein in the presence of an acid catalyst with a scavenger compound that contains a reactable thiol or hydroxyl moiety to form an acrolein derivative. The acrolein content in the refined process stream can be effectively reduced to less than about 5 parts per million.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is directed to a process for separating acrolein from an acrolein-containing process stream. In a first preferred embodiment, the acrolein-containing process stream further includes acrylonitrile and more preferably is a unrefined acrolein-containing process stream further including acrylonitrile, cyanide compounds, and potentially other byproducts and contaminants that are generated as part of an acrylonitrile manufacturing process. The specific composition of the preferred process stream will depend on a number of factors, including but not limited to the acrylonitrile reaction chemistry utilized in the acrylonitrile generating process and the specific step in the formation process at which the stream is generated. Most preferably, the process stream is generated as part of a process for manufacture of acrylonitrile by the catalytic ammoxidation of propylene. To the extent the unrefined process stream contains

1 cyanide compounds, it is particularly preferred that they be substantially removed from
2 the stream prior to the reaction step discussed in detail below wherein a scavenger
3 compound reacts with the acrolein in the stream such that the reaction step is performed
4 in the substantial absence of a cyanide compound.

5 In a second embodiment, the acrolein-containing process stream further includes
6 acrylic acid and more specifically is an acrolein-containing process stream further
7 including acrylic acid, and potentially other byproducts and contaminants that are
8 generated as part of an acrylic acid manufacturing process.

9 The process of the present invention includes reacting acrolein that is present in
10 the acrolein-containing process stream with a scavenger compound that contains a
11 reactable thiol or hydroxyl moiety to form an acrolein derivative. In a first preferred
12 embodiment, the process includes reacting acrolein that is present in the acrolein-
13 containing process stream with a scavenger compound that contains a reactable thiol
14 moiety. A thiol moiety is defined herein as the moiety $-SH$. Any chemical compound
15 containing a thiol moiety that is sufficiently soluble to facilitate reaction thereof with the
16 acrolein (preferably a compound characterized by a solubility of at least 1% by weight in
17 the process stream) in the acrolein-containing process stream is useful in the process of
18 the present invention, including mercaptoacetic acid, 2-mercapto ethanol, 2-
19 aminoethanethiol and ethylene glycol bithioglycolate. A particularly preferred
20 compound is mercaptoacetic acid. In this preferred embodiment, the acrolein derivative
21 formed by the process of the present invention is an acrolein thioacetal.

22 In a second embodiment, the process of the present invention includes reacting
23 acrolein that is present in the acrolein-containing process stream with a scavenger
24 compound that contains a reactable hydroxyl moiety. A hydroxyl moiety is defined
25 herein as the moiety $-OH$. Any chemical compound containing a reactable hydroxyl
26 moiety that is sufficiently soluble to facilitate reaction thereof with the acrolein
27 (preferably a compound characterized by a solubility of at least 1% by weight in the
28 process stream) in the acrolein-containing process stream is suitable for the process of the
29 present invention, including but not limited to alcohols, diols, glycerol, polyols, phenols,
30 hydroxy acids, hydroxy nitriles, hydroxy esters and the like. A preferred compound is
31 lactic acid. In this embodiment, the acrolein derivative formed by the process of the

1 present invention is an acrolein acetal. In this embodiment, it is preferable that the
2 acrolein-containing process stream includes water, more preferably a water content of
3 about 2% to about 3% by weight at commencement of the reaction step. Even more
4 preferably, the water content of the process stream is reduced during the reaction step to
5 no more than about 0.5% by weight water. Accordingly, in this embodiment the process
6 preferably further includes reducing the water content of the process stream to no more
7 than 0.5% water by weight.

8 The reaction step in the process of the present invention is performed preferably
9 at a pH of between about 3.0 and about 7.0, preferably in the presence of an acid catalyst.
10 The acid catalyst may be a liquid or a solid acid catalyst. Examples of the former are
11 glycolic acid and acetic acid. Examples of solid acid catalysts include polymer based
12 catalysts and ion exchange resins such as functionalized styrene divinylbenzene
13 copolymers with sulfuric acid type functional groups. Suitable catalysts are sold under
14 the AMBERLYST® trademark by Rohm and Haas.

15 In a first preferred embodiment, the acid catalyst is already present in the
16 acrolein-containing process stream, such that the process stream includes an acid catalyst.
17 For example, in the embodiment wherein the acrolein-containing process stream further
18 contains acrylonitrile and is a stream that is part of an acrylonitrile manufacturing
19 process, the acid environment may be created by the presence of acid added in an
20 upstream hydrogen cyanide purification column to inhibit hydrogen cyanide
21 polymerization. In a second embodiment, the acid environment is created by the
22 presence of an added acid catalyst and the process of the present invention further
23 includes adding an acid catalyst to the process stream prior to the reaction step. Preferred
24 acid catalyst for this embodiment includes glycolic acid and acetic acid, with acetic acid
25 being particularly preferred. It is also particularly preferred to select a scavenger
26 compound that is an acid to further establish the acidic environment for the reaction.

27 The reaction of the acrolein with the scavenger forms, in addition to the acrolein
28 derivative, a refined process stream containing the acrolein derivative. Preferably, the
29 refined process stream includes no more than 5 ppm unreacted acrolein.

30 Preferably, the process of the present invention further includes separating the
31 acrolein derivative from the refined process stream. Suitable methods for this removal

1 step will be readily apparent to one of ordinary skill in the art and will be selected based
2 on many factors, including, for example, the chemical structure of the acrolein derivative
3 (e.g., acrolein acetal or acrolein thioacetal). Suitable separation methods include
4 distillation, with utilization of existing equipment present in the overall manufacturing
5 process being particularly preferred. The following examples, while not intended to limit
6 in any way the scope of the process of the present invention, are set forth to further
7 illustrate its various embodiments and demonstrate its usefulness.

8 **EXAMPLE 1**

9 To demonstrate the utility of scavenger compounds containing hydroxyl moieties
10 in the process of the present invention, a solution containing 95 wt % acrylonitrile, 5 wt.
11 % acetic acid, 155 ppm (wt) acrolein and 500 ppm (wt) phenothiazine as a non-phenolic
12 polymerization inhibitor was made. The acrylonitrile that was used was first distilled to
13 remove most of the water and hydroquinone mono methyl ether inhibitor. The water
14 concentration of the acrylonitrile for each of these tests was 0.3 wt %. The acrolein was
15 also flash distilled to remove the hydroquinone mono methyl ether inhibitor prior to use.

16 0.1g of each of the hydroxyl-containing scavenger compounds listed in Table 1
17 below was then added to separate 10 gram samples of the above solution and the
18 resulting mixtures were placed in an oven at 50° C for the period of time indicated in
19 Table 1. The results of the test are detailed in Table 1 below:
20

Table 1

	Acrolein	Time	Acrolein	Acrolein	Time	Acrolein	Acrolein
ACR Scavenger	Initial	Hrs.	at Time	% Change	Hrs.	at Time	% Change
Ethanol	155	24	130	-16.13	96	119	-23.23
Butanol	155	24	146	-5.81	96	116	-25.16
Ethylene glycol	155	24	143	-7.74	96	110	-29.03
Propylene glycol	155	24	145	-6.45	96	116	-25.16
Diethylene glycol	155	24	153	-1.29	96	132	-14.84
Glycerin	155	24	152	-1.94	96	114	-26.45
Glycolic acid	155	24	146	-5.81	96	120	-22.58
Lactic acid	155	24	129	-16.77	96	110	-29.03

As demonstrated by the results above, the process of the present invention can remove essentially all of the acrolein from acrolein-containing process streams. The remaining acrolein can then be removed by existing refining trains such that the final concentration is less than 5 ppm and possibly as low as 1 ppm. It is recognized that, in view of these results, the extent of the acrolein removal achieved when a scavenger compound containing a hydroxy 1 moiety is utilized in the process of the present invention may not be sufficient for some end-use applications of the refined process stream.

EXAMPLE 2

To demonstrate the utility of scavenger compounds containing thiol groups in the process of the present invention, a solution containing 99.7 wt % acrylonitrile, 0.2 wt. % acetic acid, 1067 ppm (wt) acrolein was made. No polymerization inhibitor was added. The acrylonitrile that was used was first distilled to remove most of the water and hydroquinone mono methyl ether inhibitor. The water concentration of the acrylonitrile in these tests was 0.4 wt %. The acrolein was also flash distilled to remove the hydroquinone mono methyl ether inhibitor prior to use.

0.025 grams of each of the thiol-containing scavenger compounds listed in Table 2 below was added to separate 10 gram samples of the above solution. The resulting mixture was placed in an oven at 65°C for the period of time indicated in Table 2. The results of the test are detailed in Table 2 below:

Table 2

	<u>Acrolein</u>	<u>Time</u>	<u>Acrolein</u>	<u>Acrolein</u>
<u>Acrolein Scavenger</u>	<u>Initial</u>	<u>Hrs.</u>	<u>at Time</u>	<u>% Change</u>
1,2-Ethanedithiol	1067	24	322	-69.82
Mercaptoacetic acid	1067	24	9	-99.16
2-mercaptoethanol	1067	24	59	-94.47
2-aminoethanethiol	1067	24	8	-99.25
Ethylene glycol bisthiglycolate	1067	24	48	-95.50

As demonstrated by the results above, the process of the present invention effectively removes acrolein from acrolein-containing process streams. Notably, preferred scavenger compounds containing thiol groups achieve acrolein removal that is necessary for the most critical end use applications for the refined process stream. [Do we have any examples where the final concentration is less than 5ppm?]

EXAMPLE 3

To further demonstrate the utility of scavenger compounds containing thiol groups in the process of the present invention as well as the impact of scavenger solubility in the unrefined process stream on the result, a solution containing 99.6 wt % deionized water, 0.2 wt. % acetic acid, 1000 ppm (wt) acrolein was made. 0.04 grams of each of the thiol-containing scavenger compounds listed in Table 3 below was added to separate 10 gram samples of the above solution. The resulting mixture was placed in an oven at 65°C for the period of time indicated in Table 3. The results of the test are detailed in Table 3 below:

Table 3

	<u>Acrolein</u>	<u>Time</u>	<u>Acr lein</u>	<u>Acrolein</u>
<u>Acrolein Scavenger</u>	<u>Initial</u>	<u>Mins.</u>	<u>at Time</u>	<u>% Change</u>
1,2-Ethanedithiol*	1000	30	0	-100
Mercaptoacetic acid	1000	30	0	-100
Ethylene glycol	1000	30	0	-100
Bisthiglycolate*				

* denotes formation of precipitate

As demonstrated by the results above, the process of the present invention effectively removes acrolein from acrolein-containing process streams. Notably, mercaptoacetic acid demonstrated particularly desirable solubility in the subject acrolein-containing process stream by producing an acrolein reaction product that remained in solution and did not precipitate,

While the present invention has been described and exemplified in detail herein, it is to be understood that various modifications and variations thereto may be made without departing from its spirit and scope.